

Hydrogen Workshop

November 14th, Vancouver, BC

British Columbia Institute of Technology

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HYDROGEN WORKSHOP
November 14th 1998
British Columbia Institute of Technology
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A workshop on hydrogen was convened in Vancouver. Representatives with expertise in hydrogen production, storage, transportation, usage and safety contributed their ideas and visions for the GHG-mitigating energy technologies and systems pertaining to hydrogen in the 2020-2050 time frame. The main technological barriers and R & D priorities pertaining to the implementation of a hydrogen infrastructure were identified. The role of Canada and its hydrogen niche in the global marketplace was discussed.

Participants

- Prof. John Barclay, Cryofuels Systems Group, Department of Mechanical Engineering, University of Victoria (Storage and transportation of hydrogen)
- Joachim G. Borck, Senior Technologist, Daimler-Ballard Benz Fuel Cell Engines Inc. (systems engineer, fuel cells, direct hydrogen internal combustion engines)
- Stephen Brydon, Strategic Industries Branch, B.C. Trade and Investment Office, British Columbia Ministry of Employment and Investment (Canadian Hydrogen Association)
- Dr. Stephen Campbell, Senior Scientist, Core Technology, Ballard Power Systems (Chemist, fuel cells)
- Paul Howard, Consultant and Founder Member, Ballard Power Systems (Fuel cells)
- Dr. R. Ellis Knowlton, Manager, HAZOP and Consultancy Services, Kvaerner Canada Inc. (Hydrogen production, hydrogen safety)
- Pierre Rivard P.Eng., President, Hydrogenics Corp., Toronto (Fuel cells)
- David Shepherd, Senior Analyst, Science and Technology Branch, British Columbia Information, Science and Technology Agency (Canadian Hydrogen Association)
- Dr. Jurgen Stumper, Senior Scientist, Core Technology, Ballard Power Systems (Fuel cells)
- Colin Oloman, Professor of Chemical Engineering, Dept. Chemical and Bio-resource Engineering, University of British Columbia (Hydrogen production and utilisation)

INTRODUCTION

The drivers for change have to be clearly defined. Fossil fuel depletion and the need to mitigate the risk of climate change disruption caused by green house gases are seen as the two fundamental drivers that will demand the introduction of hydrogen systems.

Any approach to solving energy-related pollution problems, such as urban air pollution and global climate change, must address the issue of using fuels efficiently and with minimal emissions. Among the alternative fuels, hydrogen offers perhaps the most compelling environmental benefits.

VISION

In 2030-2050 the group considered that the ideal would be to have fossil-free, clean, reliable power generated from sustainable, clean, reliable energy sources.

HYDROGEN IN CONTEXT-ITS LONG-TERM ROLE

Electricity will still be the prime energy carrier 2030-2050 because it is the most valuable and flexible, form of energy for society. Like electricity, hydrogen is a premium quality energy carrier, which can be used with very high efficiency and zero emissions.

However, it is more than a carrier, it is both an energy distribution and storage system-a currency that allows energy transactions. In situations when there is an oversupply of electricity that cannot be stored by using advanced battery, or other systems, the electricity can be converted to hydrogen for storage. Fuel cells and electrolysis are necessary for neutral conversion of electrical energy and hydrogen.

Hydrogen can be produced from any energy source and will inevitably be produced from sustainable sources - it is never an energy source itself. Many consider the future lies in solar and nuclear energy with a hydrogen distribution system. However, there are other alternatives, often locally available, sustainable energy sources such as biomass, hydro, wind, geothermal and tide. Another sustainable option would be to produce hydrogen from fossil fuels if all the carbon could be separated and sequestered.

Hydrogen transportation, heating and power generation systems have been technically demonstrated, and in principle, hydrogen could replace current fuels in all their present end-uses. If hydrogen were made from renewable, nuclear or decarbonised fossil sources, it would be possible to produce and use energy on a large scale with no emission of greenhouse gases or pollutants. Although hydrogen energy systems offer environmental benefits, there are significant technical, cost and infrastructure challenges, which must be met before they could be widely used.

The negative side of hydrogen consumption is the energy needed to produce it and to provide for energy losses in the hydrogen-to-application chain. With existing technology, hydrogen requires at least twice as much energy as electricity-twice the tonnage of coal, twice the number of nuclear plants, or twice the number of PV panels to perform the equivalent amount of work. Much of this energy investment is in the hydrogen production step.

HYDROGEN PRODUCTION

The hydrogen infrastructure drivers must be considered. Should hydrogen be produced from stationary local sources or should it be transported? Should reformers or water electrolysis be considered?

Currently, very little (5%) of the hydrogen produced commercially is available as "merchant hydrogen." The other 95% is used on-site at the refinery or chemical plant where it is produced. Hydrogen is widely used in the petroleum refining processes such as hydrotreating, catalytic reforming, and hydrocracking. It is a raw material for

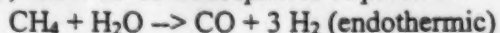
innumerable chemical processes ranging from the manufacturing of high-density polyethylene and polypropylene resins to the hydrogenation of food-grade oils. It is also used in the electronics industry in the manufacture of silicon wafers and computer chips. Hydrogen is used as rocket fuel. It will be the demand for hydrogen as a clean fuel that will increase the proportion of merchant hydrogen produced. In 1998, world hydrogen production totalled about 40 million tonnes, which represents 1% of the world's energy demands. The 5% availability of "merchant hydrogen" would be sufficient to fuel 100,000 buses or 5 million fuel cell vehicles.

Most of today's hydrogen is produced from natural gas—this can only be an interim solution since it discards 30% of the energy in a valuable, but depletable fuel (natural gas) to obtain 70% of another (hydrogen). The challenge is to develop more appropriate methods based on sustainable energy sources, methods that do not employ electricity as an intermediate step.

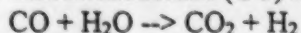
Hydrogen can be produced by several methods from many different feedstocks, including: steam-methane or other steam-reforming systems e.g. methanol; partial oxidation; water electrolysis; dissociation of ammonia; and recovery from by-product streams from chemical manufacturing and petroleum reforming. However, the production and processing of hydrogen is not pollutant free, especially if the hydrogen is produced from natural gas, and is liquefied rather than compressed for on-board storage. To properly evaluate hydrogen production methods, the environmental impact must be considered over the total production lifecycle i.e. the type of energy source must be considered. The use of compressed hydrogen from water electrolysis, (using nuclear power or a renewable source) offers an 80-90% reduction in emissions of GHGs, whereas the use of liquid hydrogen made from water electrolysis only offers a 50%-60% GHG reduction. The use of compressed hydrogen from natural gas offers only a 30% reduction in GHGs, and the use of liquid hydrogen from natural gas offers essentially no GHG benefits.

Large-scale production

Steam methane reforming. The most well-established method for large-scale hydrogen production is steam methane reforming (SMR). Steam methane reforming is a three-step process. First, methane (natural gas is essentially methane from which impurities such as sulphur have been removed) is reacted with steam over a catalyst which produces a mixture of carbon monoxide and hydrogen (syngas). Large reformers operate at about 850°C, under 15-25 atmospheres of pressure.



In the second step, after the products are cooled, a shift reaction takes place where most of the carbon monoxide (CO) reacts with steam to generate hydrogen and carbon dioxide:



The gas exiting the shift reactor is typically 70% hydrogen and 25% CO₂, with a few percent methane and less than 1% CO (on a dry basis). For hydrogen production, the third crucial step of gas separation, following steam reforming or partial oxidation, can be

accomplished commercially with technologies based on adsorption, absorption, or membrane separation. The most common commercial process is pressure swing adsorption (PSA), where carbon dioxide is selectively adsorbed, usually on activated carbon. During PSA the hydrogen can be purified for final delivery to yield a purity near 99.999% if required. The absorption process of amine scrubbing is commonly used for removal of carbon dioxide from natural gas, and this technique also can be applied to hydrogen separation. Advanced membrane technologies are being developed that may prove to be superior to both of these processes. Further in the future lie clathrate-based and other advanced-separation technologies.

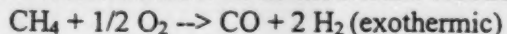
SMR is prevalent because natural gas is relatively inexpensive and plant capacities for the size of a small refinery are about 50 tonnes/day (the average hydrogen requirement for a fuel cell vehicle is about 1 kg/day). SMR plants are able to operate non-stop for about five years, thus operation and maintenance is minimal, and start-up and wind-down costs are proportionately small. Since SMR is likely to remain important for some years to come it will be important to increase the efficiency of this process by: a) reducing the amount of excess steam produced; and b) utilising effectively the steam that is produced. Improved heat exchanger materials and better catalytic materials that are more tolerant to impurities, such as sulphur, would also yield significant process improvements. Although, SMR produces the cheapest hydrogen on the market (1999 costs-\$850/tonne for small refinery production of 45 t/day to \$700/tonne for the largest plant in existence producing 450 tonnes/day), until the carbon dioxide from this process is captured and sequestered the environmental costs are high. In fact they almost negate the zero-emission combustion advantages of hydrogen.

Gasification of coal or biomass, with low-cost separation of CO₂ and permanent sequestration underground, for example in depleted gas wells or deep aquifers has been suggested as another option for large-scale hydrogen production. If this type of "fuel decarbonisation" were coupled with CO₂ sequestration, fossil energy could be used with significantly reduced greenhouse gas emissions. However, the proponents of a "hydrogen economy" consider any use of fossil fuels as unacceptable and a temporary solution at best.

The energy for the steam reforming process has to be generated. Efficiency concerns dictate that as much heat as possible is recovered and returned to the steam reformer. However, significant energy is lost in the SMR process -the smaller the steam reformer the larger the proportionate energy loss. The worst GHG emission case would occur if fossil fuels were used to generate energy without any carbon dioxide capture and sequestration either during energy generation or the SMR process. However, it is possible to link SMR with electricity from non-carbon sources.

Partial Oxidation Partial oxidation reactors are simpler devices than steam reformers and are suitable for making hydrogen from a wider range of fuels. Partial oxidation is used at large scale to produce hydrogen at some refineries, operating with relatively pure oxygen as the oxidiser, rather than air. Like SMR, partial oxidation is also a three-step

operation. In a partial oxidation reactor natural gas is combined with oxygen which produces carbon monoxide in an exothermic reaction.



The second two steps in partial oxidation are the same as steam reforming.

A variety of feedstocks can be used for partial oxidation including: solar heated organic waste; landfill waste etc. Under certain circumstances partial oxidation can lead to direct hydrocarbon splitting yielding carbon black which can be used for carbon-fibre feedstock.

Non-fossil generation. Large-scale, non-fossil hydrogen generation is still considered to be embryonic. Nuclear and hydro-electric power are the only large-scale, commercially proven, non-carbon electricity sources. They can also provide the high-capacity base needed to stabilise electricity grids so they can accommodate other non-carbon lower-capacity sources such as wind and solar. "Non GHG electricity" from a nuclear or hydraulic plant, supplemented by electricity from renewable sources, could be used to power stand-alone hydrogen production facilities.

The opportunity exists to use nuclear or hydro-electric energy sources to produce DC electricity directly without an intermediate AC step. This could improve the efficiency of DC electricity production by up to 5%. These units could interrupt their DC current to produce electrolytic hydrogen, to produce "peak shaving" AC for the electricity grid.

Power from nuclear fission will have a finite lifetime until such time as safe breeder reactors can be developed. If breeder reactors cannot be made with any degree of efficiency then the nuclear fission business may not be so attractive because it will run out of uranium and thorium fuel within about thirty years. Disposal and/or transmutation of radioactive waste is also a problem to be faced. The current thinking on nuclear reactors is that they can be operated safely. Instead of having 1,000 MW reactors, ten 100 MW reactors could be built. One suggestion to decrease operational risks is to float reactors in lakes containing elements of high cross section in which they could be sunk if a problem occurred to extinguish their nuclear fire.

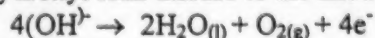
Another long-term energy strategy is to develop nuclear fusion. Currently, hot fusion reactors have only functioned for a couple of seconds. Cold fusion remains a possibility but is probably a technology for the second half of the twenty-first century.

In the long-term space-based solar power, beamed to earth as microwaves, might be a large-scale source of non-fossil energy that could be used to produce hydrogen. NASA claims it will have a demonstration project in operation by 2010 based on a solar tower. It has been suggested that an array of solar reflectors on the moon could ably perform the task of increasing the solar intensity beamed to earth. Other ways of utilising energy from other planets, such as utilising their geothermal energy was contemplated in the consideration of energy sources. In making use of these sources a cautionary note was sounded about the importance of not upsetting the equilibrium of "system earth."

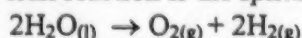
Electrolysis Water electrolysis requires only water and electricity to generate hydrogen. A conventional electrolysis cell has two electrodes that are maintained at a positive (anode) and negative (cathode) potential respectively. The two electrodes are immersed in an electrolyte-usually an aqueous solution of potassium hydroxide. The potassium hydroxide is a conductor that facilitates the ionisation of water into hydrogen and hydroxyl ions. The reaction at the cathode is the reduction of water to generate hydrogen and hydroxyl ions:



The hydroxyl ions diffuse to the anode where they are oxidised to liberate oxygen:



The overall reaction is the splitting of water into its elements:



The two gaseous streams can be collected and the hydrogen, which is extremely pure after water has been extracted from it, can be used to power fuel cells. The rate of hydrogen production is increased when catalysts are added to the electrode surfaces. Increasing the temperature of the reaction can also increase the efficiency of electrolysis. In practical terms the amount of electricity for the process can be greatly reduced by increasing the temperature of reaction. In a typical electrolyser there is a separator (often asbestos for an alkaline cell) to keep the products of electrolysis from mixing-it is the inability of the separator to withstand high temperatures that often determines the upper-bound temperature.

Many developments are taking place to produce better electrolyzers. Advanced water electrolysis (AWE) uses inorganic membranes for the separator and more expensive materials throughout the electrolytic cell, to withstand higher heat and high temperature alkaline corrosion.

In the early seventies General Electric showed that the proton exchange membrane (PEM) fuel cell could be modified to act as a PEM electrolyser. The PEM electrolyser is a solid polymer electrolyser. It is more compact than an alkaline cell and does not contain corrosive liquid. However, its component parts are expensive and at present these electrolyzers are used in niche applications where size is important, such as in aerospace and military applications. In the long-term they could be important not only just as electrolyzers or fuel cells but as reversible devices that can produce hydrogen or electricity on demand.

The solid oxide electrolyser is a high temperature electrolysis (HTE) device. It operates at about 900-1000°C and the efficiency of the device is tied to the existence of a heat source. HTE uses vaporised water and a solid electrolyte, which conducts oxygen ions. HTE is potentially an important long-term technology for hydrogen production.

The efficiency of electrolyzers varies from about 77-80% for the conventional alkaline device to between 90-100% for a high temperature (water vapour) electrolyser.

Under certain circumstances, in addition to oxygen the by-products from electrolysis can include heavy water (deuterium oxide). A Canadian technology for heavy-water

recovery during electrolysis looks promising. In the case of CANDU nuclear reactors, the hydrogen streams can be preprocessed to recover trace concentrations of deuterium, which can be re-oxidised to heavy water. The efficiency of the hydrogen, heavy-water process is close to 75%.

The importance of continuing efforts to improve the flexibility, and to lower capital and operating costs of electrolytic hydrogen production, is clear. Because electrolysis is inherently modular, scale-up uncertainties are reduced. However, it may well be that a central production and generation scheme similar to that of oil or natural gas today is inherently more expensive than one that relies on a distributed network of on-site hydrogen production plants. Electrolysers could represent an exception to economies of scale. Currently, the capital costs of electrolysers are far higher, for comparable capacity units, than steam reformers or partial oxidation units.

There are one or two examples of hydrogen made at large-scale via electrolysis of water at some dams, using low-cost off-peak power. Electrolysis is a competitive route to hydrogen only when electricity is inexpensive, a situation that may occur with off-peak pricing. An expanded role for electrolysis will require lower-cost electrolysers; one approach could be to use the fuel cell in reverse to produce hydrogen at off-peak times, and then to produce electricity from the stored hydrogen at on-peak times.

Other hydrogen production methods

Thermochemical Thermochemical production of hydrogen (efficiency approximately 50%) uses heat to decompose water. Thermochemical processes typically have three steps, including oxygen production, hydrogen production and materials regeneration. The multiple-step approach enables the water splitting to take place at approximately 700°C rather than the 2,500 degrees that would be needed in a one-step process. The Japanese have achieved stable hydrogen production from thermochemical water splitting with a high-temperature gas-cooled nuclear reactor using the iodine sulphur process. This process is not efficient and there are many problems associated with high temperature erosion/corrosion of the reactor components.

Direct hydrocarbon splitting Under the extremely high temperature conditions of a plasma arc it is possible to split hydrocarbons directly. Hydrogen and carbon black, which holds commercial value as a feedstock for other chemical processes, are produced.

Photochemical and photoelectrochemical processes Photochemical processes involve the use of solar energy to split water. Photovoltaics can be used to produce electricity, which is then used for water electrolysis. Photovoltaic materials do not as yet have a high degree of efficiency (10-20%), however, there is a large research effort in the U.S. and Japan to improve semi-conductor- and biologically-based photovoltaic materials, and to widen the portion of the electromagnetic spectrum that can be utilised by these devices. Thin film solar cell technology appears to hold promise.

In contrast, photoelectrochemical devices provide "one-stop shopping" for hydrogen and electricity. The two steps of converting sunlight to electricity, and electricity to hydrogen, are combined into a single process without the use of an external power source. A solar water splitter consists of a semiconductor sandwich that is immersed in water. In the splitter two different semiconductor materials produce electric charges with exactly the right energy to catalyse the water-splitting reaction to produce hydrogen and oxygen. Gallium indium phosphide absorbs visible light and ultraviolet and produces mobile electrons with the right energy to produce hydrogen. Gallium arsenide absorbs infrared and produces holes with the right amount of energy to produce oxygen. Gallium indium phosphide is stable in water so it can be used directly as an electrode, however, gallium arsenide is unstable in water and has to be sealed with a transparent epoxy coating through which the holes are shuttled to a platinum electrode. The process seems to be stable and efficient -the cost is high but holds a lot of potential for hydrogen production in the 2030-2050 time frame. Development of cheaper semiconductor materials that perform the same function is key in bringing the cost down.

Biological and photobiological processes Under the right circumstances hydrogen can be generated directly from water by biological or biochemical means.

Photobiological generation of hydrogen involves the activation of biological organisms in water (e.g. bacteria and algae) by sunlight. Atmospheric carbon dioxide is fixed by this mechanism and the water reduction results in hydrogen and oxygen being produced. It is a similar process to photosynthesis, the difference being that a carbohydrate (hydrocarbon) is not produced. The possibility of genetically engineering organisms to increase hydrogen production, as well as using solar concentration devices such as fibre optics, would improve a process that has a very low (<0.1-5%) solar conversion efficiency. Biological technologies were felt to hold promise because they will be inexpensive.

Biological means can be used to clean up gaseous fuels. Bacteria can be used as low-temperature catalysts to produce carbon-monoxide free hydrogen. This is a process that mimics the shift reaction in reforming or partial oxidation where carbon dioxide reacts with steam to produce hydrogen and carbon dioxide.

Biomass Producing hydrogen from biomass involves either biological or chemical conversion of the biomass. The biological process generally involves a number of stages to produce a hydrocarbon from which hydrogen is extracted. The hydrocarbon is produced by anaerobic digestion while the hydrogen extraction typically involves steam reforming. This last part of the process is the main hurdle for biological processes because steam reforming requires large amounts of energy that makes the process uneconomical. Generally, biomass is considered to be a distributed energy source, produced and processed close to where it is harvested. Small-scale steam reforming becomes very costly because of inability to recover the heat from the steam, and the dominance of capital outlay costs for the reformer. Chemical conversion of biomass, besides being expensive, produces emissions in the form of tars, phenols and acids.

Candidate biomass materials include: a) crops grown specifically to generate hydrogen; b) animal wastes; c) human wastes of which sewage and industrial wastes from foods or chemical processes are a possibility. The key to improving efficiency was felt to lie in shortening the lifecycle of candidate biomass materials.

By-product It should not be forgotten that hydrogen is recovered from by-product streams from chemical manufacturing and petroleum reforming

GROUP PREDICTIONS FOR 2030-2050 HYDROGEN PRODUCTION AND PURIFICATION

Energy source - non-fossil "clean" sources

- Space-based solar
- High focussed solar
- Nuclear to produce high temperatures
- Cold fusion
- Energy from other planets
- Hydropower
- Geothermal energy

Processes

- Electrolysis
- Partial oxidation
- Steam methane reforming: natural gas, biomass etc.
- Anaerobic direct generation of hydrogen
- Reverse fuel cell
- Photoelectrochemical cell
- Plasma-arc hydrocarbon splitting
- Byproduct of industrial processes

Purification

- Membranes
- Chemical and physical adsorption (such as pressure swing absorption)

Two long-term, low-energy hydrogen production processes that hold potential are:

- direct conversion of biomass to hydrogen because it bypasses the electricity step; and
- direct sunlight methods where photon-catalysed hydrogen production occurs without involving electrolysis.

HYDROGEN STORAGE AND TRANSPORTATION

Like electricity, hydrogen storage presents a challenge. Electricity stored in batteries, capacitors, or magnetic coils is bulky, heavy, inefficient, or short lived. Hydrogen storage in compressed-gas containers, in metal hydride beds, or in dewars as a liquid suffers from one or more of these shortcomings. A storage approach is needed that can preserve hydrogen's lightweight and energetic qualities and minimise its bulky nature.

Investigation into the adsorptive properties of carbon in the form of nanotubes, carbon platelets in a herringbone formation-essentially nanowhiskers, and fullerenes is producing some interesting results that could result in rechargeable hydrogen cartridges. This technology would solve a lot of the problems associated with the hydrogen infrastructure needed for hydrogen to have widespread use in the transportation field.

Large-scale production of hydrogen implies that an infrastructure has to be in place for storage and distribution-particularly for transportation use. The goal of any storage mechanism for hydrogen is to enable large amounts of the gas to be stored and transported safely, effectively and economically. Hydrogen can be stored as a compressed gas, liquefied and stored cryogenically as a liquid or as slush hydrogen, or stored in a solid medium such as carbon or as a metal hydride. Each of these storage methods has its drawbacks. Hydrogen storage is extremely important because hydrogen provides a practical storage medium for excess electricity when the amount to be stored is too large to make rechargeable batteries a practical alternative.

Compressed gas and liquid hydrogen

Hydrogen can be compressed and stored at about 5,000 psi in lightweight metal (e.g. aluminum) containers wrapped with composite materials to give them strength. It is usually stored on-board a vehicle at 3,600 psi as fuel for a fuel cell. Energy is required to compress the gas; however, it is not as much as the energy needed to liquefy hydrogen. The energy required for hydrogen liquefaction expressed in MJ per MJ of hydrogen is 0.30 compared with 0.05 for compressed hydrogen. This means that 30-35% of the energy value of the fuel is lost in the liquefaction process. The temperature of liquid hydrogen is only about 20 degrees above absolute zero, which make it difficult to store for any length of time without considerable loss of the product through boil off. The energy density of compressed hydrogen gas at 5,000 psi is comparable with that of liquid hydrogen, the disadvantage of gaseous hydrogen is its bulk.

Distribution of gaseous hydrogen can be effected through dedicated hydrogen pipeline systems or by spiking natural gas in existing pipelines by addition of 10-12% hydrogen. Currently, there are some dedicated hydrogen pipelines: about 210 km in the Ruhr Valley in Germany; a 400 km line between Belgium and France; and some small local pipelines in Canada and in Los Angeles and Houston in the U.S. These dedicated pipelines are expensive to build and local. It has been estimated that it would cost 100 billion dollars to replace Canada's natural gas pipeline system, presumably the cost of constructing a dedicated hydrogen pipeline system would be comparable. Thus, the capital outlay for a new hydrogen pipeline system would be prohibitive.

Adding hydrogen to natural gas pipelines is theoretically possible and should not be cause for any major concern so long as the hydrogen exists in molecular form. Atomic hydrogen is reactive and associated with hydrogen embrittlement and crack formation. Introduction of hydrogen into Canada's existing pipeline system would require higher-pressure pumps and a number of measures to prevent embrittlement. Canada is already facing a number of problems with its ageing pipeline system that would make the advisability of transporting hydrogen-enriched natural gas questionable.

Compressed hydrogen can also be transported by tube trailer. The problem with gaseous hydrogen is its bulk. Transporting enough hydrogen by tube trailer to supply Chicago Transit Authority's (CTA) zero-emission fleet for a month would require ten truck loads. This makes the trucking costs for the gas prohibitive. A single cryogenic tanker needs can meet CTA's supply. Chicago Transit buys hydrogen from Sarnia and trucks the liquid fuel to a commercial hydrogen fuelling station where it is stored cryogenically until needed, at this time it is vaporised and stored on-board the buses at 3,600 psi for injection into a fuel cell stack.

Currently, the main ways to produce and deliver gaseous hydrogen as a transportation fuel are:

- 1) hydrogen produced from natural gas in a large, centralised steam reforming plant, and truck delivered as a liquid to refuelling stations
- 2) hydrogen produced in a large, centralised steam reforming plant, and delivered via small-scale hydrogen gas pipeline to refuelling stations,
- 3) by-product hydrogen from chemical industry sources,
- 4) hydrogen produced at the refuelling station via small scale-steam reforming of natural gas, and
- 5) hydrogen produced via small-scale electrolysis at the refuelling station.

The capital cost of infrastructure and the delivered cost of hydrogen need to be estimated for each hydrogen supply option.

It is possible to transport liquid or slush hydrogen in pipelines but it is extremely expensive and unfeasible over for anything but extremely short distances. Perhaps with the advent of better superconducting materials it would become more feasible to transport liquid hydrogen over longer distances in pipelines.

Another alternative would be to have a closed-loop pipeline system, in which hydrogen is combined with a carrier at one end, transmitted to the other end, where the compound is dehydrogenated and recycled for further use. A commercially feasible proposal for this approach has been demonstrated. A light metal hydride/organic slurry (light mineral oil) is used as the hydrogen storage medium. At the point of storage and use a metal hydride/water reaction is used to produce high-purity hydrogen. An essential feature of the approach is the recovery and recycle of the spent hydride at central processing plants. This approach has two clear benefits: it greatly improves energy transmission and storage characteristics of hydrogen as a fuel; and the hydrogen carrier is produced efficiently and economically from a low-cost carbon source. Calcium, sodium and lithium hydrides; sodium boron hydride; and lithium boron hydrides have been investigated. Lithium boron hydride holds promise for yielding the greatest proportion of hydrogen.



Rail or ship for the long haul can transport both liquid and gaseous hydrogen. The key hurdle to overcome with liquid hydrogen or slush hydrogen is fuel boil off. Boil off occurs if hydrogen is left sitting in a cryogenic tank. The fuel essentially heats up, expands and increases in pressure until it is released through a relief valve. The best

technology for storing liquid hydrogen is a magnetic levitation device where an interior tank that holds the actual fuel is suspended magnetically inside the outer shell, without any of the struts normally need to fix the inside tank in place. With no mechanical linkages, other than the filler tube and the "fuel line" from the tank to the motor (ICE or fuel cell) heat influx to the tank and boil off rates are greatly reduced. This type of tank can currently store hydrogen at -253°C with virtually no boil off for three to four days which represents a 50% improvement over conventional dewar vessels.

Carbon nanotubes There is a significant research effort into using the adsorptive and absorptive properties of carbon for hydrogen storage.

There are reports of microscopic graphite fibres, or "carbon whiskers", made up from stacks of platelets that can soak up a considerable amount of molecular hydrogen per gram of carbon-about 45% hydrogen storage by weight. If true, and there is a lot of scepticism concerning the repeatability of the results, this would represent a real breakthrough in storage technology. Preliminary numbers indicate that sufficient hydrogen for a fuel cell car to travel about 8,000 km could be stored in a tank about half the size of a current gasoline tank. It would mean that you would be able to buy a cartridge of hydrogen instead of having to fill your car up at a filling station. In this particular technology in which graphene layers are formed in a herringbone pattern, the pretreatment of the molecularly-designed solid is crucial in ensuring the storage of hydrogen between the platelet layers. As is the pressure and temperature of the hydrogen-uptake process. Hydrogen appears to push the platelet layers apart forming a triangular matrix next to the carbon with a hexagonal, closely-packed layer of "solid" hydrogen on top of the triangular array. The time to commercialisation of this particular technology is estimated to be three years (2002).

Other work on carbon adsorption has been conducted at low temperatures (77K, 150K and 293K). Nothing like the percentage weight adsorption or absorption has been demonstrated for the other forms of nanocarbon. However, carbon adsorption/absorption materials are still considered worthy of investigation because it would provide a safe and relatively compact way to store hydrogen without incurring any of the high capital costs of establishing a hydrogen infrastructure.

Metal Hydrides A new generation of low-cost metal hydrides has been developed for hydrogen storage that have good storage capacity and good kinetics for absorption and desorption. The new generation metal hydrides are based on known and new materials. The requirements of hydrogen storage are good hydrogenation/dehydrogenation kinetics at a given temperature, high-hydrogen capacity and low cost. Five percent weight absorption at less than 100°C and desorption at 1 atmosphere pressure are the stringent goals that would allow metal hydrides to be used competitively as hydrogen storage materials.

One of the drawbacks of metal hydrides is their weight. Attention has focussed on lighter metals such as magnesium and lithium-however; a high temperature is needed to release hydrogen from these materials. It has been found that intermetallic compounds such as

sodium aluminum hydride or magnesium nickel hydrides yield better properties than other hydrides, especially if titanium is used as a catalyst in the reaction. Hydrogen absorption approaching 5% by weight has been achieved with sodium aluminum hydride over a 1 h charging time.

Hydrides have been developed to complement the different operating temperatures of the various fuel cell types.

Low temperature operation (below 140°C) A family of complex alkali-based hydrides (complex sodium alanates) has been developed aimed at the requirements of proton exchange membrane (PEM) cells that operate at around 100°C. These hydrides are capable of reversible operation in the relatively low temperature range of 80-140°C with a hydrogen capacity of 2-3.5 wt. %. In the temperature range of 160-200°C they have an even higher reversible hydrogen capacity of about 5 wt. %. They are also made from low-cost materials.

Moderate temperature operation (between 130-200°C) Complex metal hydrides (new lithium-sodium alanates) have been developed, which can operate reversibly with a relatively high hydrogen capacity of up to 4.5 wt. %.

Medium temperature operation (between 190-250°C) Within this temperature range there are several families of alloys (e.g. hydrides from the magnesium-aluminum system and lithium-based complex hydrides) that are suitable for specific applications (e.g. phosphoric acid fuel cells). The family of complex lithium-based hydrides exhibits a reversible capacity for hydrogen of more than 8 wt. %.

High temperature operation (above 250°C) High hydrogen capacities of up to 7 wt. % can be obtained with magnesium-based hydrides. In addition to very fast kinetics, these hydrides are inexpensive and easy to fabricate.

The bottom line with metal hydrides is weight. For stationary use this does not present a problem. For transportation use, particularly in conjunction with a PEM fuel cell, the hydrogen absorption density would have to be sufficiently large to justify the excess weight. As stated previously, hydrides would provide a safe way of containing hydrogen for on-vehicle use.

Glass microspheres High-strength glass microspheres (essentially tiny bubbles) can be filled with high-pressure hydrogen for convenient bulk storage and transport. The walls of these microspheres, which can be 25-100 microns in diameter, are about 1 micron thick. Immersing them in a high-pressure bath of hydrogen and then raising the temperature of the glass to 200-400°C can fill them. At this elevated temperature the glass becomes highly permeable to hydrogen and the spheres fill up. Cooling the microspheres to room temperature traps the hydrogen in them. The glass microspheres then become safe, cost effective carriers for the hydrogen. Heating the microspheres again releases the hydrogen in them.

Researchers have developed a method for producing strong, defect-free microspheres, which have a hoop stress at failure of about 150,000 psi. These engineered microspheres could make the storage and transport of hydrogen much more efficient. An analysis indicates that rail transport of hydrogen in glass microspheres could be economically competitive with liquid hydrogen.

Although theoretically possible as a storage mechanism, the energy used in hydrogen infiltration of the spheres and its release and the considerable care that has to be taken throughout the production of the spheres makes the viability of storage by glass microspheres questionable. Glass microsphere technology was originally developed for nuclear fusion tests.

GROUP PREDICTIONS FOR 2030-2050 HYDROGEN STORAGE AND TRANSPORT

Storage

Local and central storage is required

- Compressed gas
- Glass microcapsules
- Liquefied (cryogenic) hydrogen
- Slurry/slush
- Nanotubes, nanofibres
- Metal hydrides (mainly for stationary use)
- New hydrogen compounds (e.g. cyclohexane)
- Biological storage

Transportation

- Pipelines for gaseous hydrogen
- Pipes or tankers for liquid hydrogen
- Teleportation (beam)
- Biophysical/biological
- Organic transporters
- Materials containing hydrogen that can be released easily

The technologies that hold promise in the long-term for compact hydrogen storage are felt to be low-temperature carbon adsorption/absorption and advanced hydride beds.

USES FOR HYDROGEN AS A CLEAN ENERGY CURRENCY

The use of hydrogen as a clean energy technology was enabled by the development of the fuel cell. A breakthrough "clean machine," the fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution.

Fuel Cells

In principle a fuel cell operates like a battery. It supplies electricity by combining hydrogen and oxygen electrochemically without combustion. Unlike a battery, a fuel cell

does not run down or require recharging. It will produce energy in the form of electricity and heat as long as fuel is supplied. The only waste product is pure water.

A fuel cell has two electrodes separated by an electrolyte. Oxygen enters the fuel cell over the cathode, and hydrogen fuel is fed into the anode. Encouraged by a catalyst, the hydrogen splits into a proton and an electron that take different routes to the cathode. The hydrogen ion (proton) migrates through the electrolyte, while the electron moves through the external circuit to the anode. This electrical current can be utilised before it returns to the cathode. At the anode the hydrogen ion combines with the electrons and oxygen to yield water and heat. To generate useful amounts of current, fuel cells are stacked like a multilayer sandwich.

A fuel cell system that includes a reformer can utilise hydrogen from any hydrocarbon fuel—from natural gas to methanol, and gasoline. Fuel cells promote energy diversity and a transition to renewable sources.

Different fuel cells use different electrolytes and operate at different temperatures. Each is best suited to a certain application. For example, polymer electric membrane (of which the proton exchange membrane cell is one example) fuel cells are thought to be best suited for cars, while molten carbonate fuel cells are likely to be well suited for use with gas turbines.

For fuel cells to be commercially viable there are performance criteria that must be met. One of these is operating life relative to capital cost. For stationary power plants, the target is 20,000 to 40,000 hours for a cost of between \$1,000-1,500 US per kilowatt. By contrast, automobile and bus operating life is 5,000 and 10,000 hours respectively for a cost of \$50 to \$250 per kilowatt. In the case of transportation, because of the limited space available for fuel supply, fuel cells must have a higher power density or power for a given size and weight, compared to stationary power plant applications where fuel efficiency is the important consideration. Currently, research is focussed on reducing the cost, weight and size of fuel cells. In the case of proton exchange membrane cells the cost, to a large extent, is determined by the cost of the platinum catalyst which is used to coat both the electrodes.

Phosphoric Acid This is the most commonly developed type of fuel cell. It is already in use in hospitals, nursing homes, hotels, schools, office buildings, utility power plants, and airport terminals. Phosphoric acid fuel cells generate electricity at more than 40% efficiency and nearly 85% if the steam from the fuel cell is used for co-generation. The operating temperature of phosphoric acid fuel cells is about 205°C. These fuel cells can be used in large vehicles such as buses or locomotives.

Proton Exchange Membrane These cells operate at relatively low temperatures 90-95°C. They have high power density, can vary their output quickly to meet shifts in power demand and are suited for applications such as automotive use where quick start-up is required. Proton exchange membrane (PEM) cells are the primary candidates for

light-duty vehicles, for buildings, and potentially for small applications like replacements for batteries in video cameras.

Molten Carbonate Molten carbonate fuel cells promise high fuel-to-electricity efficiencies and the ability to consume coal-based fuels. This cell operates at about 650°C.

Solid Oxide Solid oxide fuel cells are highly promising for big, high power applications -including industrial and large-scale central electricity generating stations. They also hold promise for motor vehicle applications. A solid oxide system uses a hard ceramic material instead of a liquid electrolyte, allowing temperatures to reach close to 1,000°C. Power generating efficiencies could reach 60%.

Other Fuel Cells Direct methanol fuel cells (DMFC) are similar to PEM cells in that they both use a polymer membrane as the electrolyte. However, in the DMFC, the anode catalyst itself draws the hydrogen from the liquid methanol, eliminating the need for a fuel reformer. Efficiencies of about 40% are expected which would typically operate at a temperature between 50-90°C. Higher efficiencies are expected at higher temperatures. The simplest way to store and transport hydrogen is as a light hydrocarbon such as methanol which has a high H:C ratio and is a liquid under ambient conditions. If the alcohol is generated by biomass fermentation, the carbon cycle is only very short term and no GHGs are produced which would not be rapidly recycled into biomass again by photosynthesis, i.e. storage of solar energy. The primordial carbon is left in the ground or at least not burnt but is still available as a valuable feedstock. DMFC technology is less than ten years from commercialisation and the infrastructure for fuel delivery is already in place. What is required is the rapid scale-up of fermentation technology to meet demand.

Regenerative fuel cells are still embryonic. They would be attractive as a closed-loop form of power generation. Water is separated into hydrogen and oxygen by a solar-powered electrolyser. The hydrogen and oxygen are then fed into the fuel cell, which generates electricity, heat and water. The water is then recirculated back to the solar-powered electrolyser and the process begins again.

Transportation

Fuel cells have the ability to power vehicles that will be quieter, cleaner and more energy efficient, with equivalent range and performance than those powered by internal combustion engines. The benefits will be high, in national energy security, cleaner air and economic opportunity. Fuel cell vehicles offer the advantages of battery-powered vehicles but can be refuelled more quickly and go longer between refuelling- in addition to their decreased "total lifecycle" (includes all emissions associated with primary resource recovery, fuel processing and use) release of GHGs.

The first breakthrough into the market came with the introduction of fuel cell "zero-emission" buses in Vancouver, Chicago and California. Many predict cars of the future will be powered entirely by fuel cells. All the major auto manufacturers have an on-

going research and development program into fuel cell vehicles for personal transport. Fuel cells could also be used for applications such as underground mine vehicles where zero emission in a confined space is critical for health reasons.

Stationary Power

Molten carbonate and solid oxide fuel cells are currently being developed for stationary power use in industrial plants, hospitals and residential applications. They are also used as back-up power units to provide uninterruptible power systems (UPS) for critical applications when the grid supply fails. Fuel cell power systems are currently being installed to provide heat and power at selected military bases in the US. They are also being developed for auxiliary power units for troops in combat.

Military "Stealth" Use

Because they are quiet, flexible, and operate at low temperatures fuel cells are ideal for use in "stealth" vehicles. They are also being developed for use in submarines, surface ships and for a variety of other military uses.

GROUP PREDICTIONS FOR HYDROGEN USAGE IN 2030-2050

1. Thermal conversion processes
2. Electrochemical conversion processes
3. Fuel for transport
4. Fuel for home/stationary use.
5. Hydrogen in chemical form will still be used to synthesise other chemicals
6. Dual-purpose membranes for recycling would have increased efficiency if hydrogen were used.
7. Superconducting motors would run with few energy losses at the temperatures of liquid hydrogen

OTHER FUNDAMENTAL TECHNOLOGIES

- Materials
- Processes
- Biotechnology
- Custom manufacturing
- Sequestration of CO_2

OVERALL PRODUCTION SCENARIOS

- Solar energy to heat organic waste to produce hydrogen in the home
- Biomass and complex hydrocarbons engineered to capture hydrogen which can be released by reforming
- Space-based solar energy which is fed to photoelectrochemical (PEC) cells
- Partial oxidation for generation of hydrogen
- Biomass used as a feed stock to produce anaerobic direct hydrogen chemical reactors

- Solar-capture facilities (e.g. roof- and wall-mounted photovoltaic panels) would provide local (off-grid) electricity for water electrolysis to produce hydrogen for home and industrial fuel cells.

OVERALL STORAGE/TRANSPORTATION SCENARIOS

- The group felt that "small is beautiful." They endorsed local energy conversion (from clean sources) or "distributed power generation" that would eliminate the need for transmission of hydrogen. They envisioned a scenario in which electricity from local sources would top-up the supply for "smart" houses equipped with solar capture facilities, perhaps photoelectrochemical cells, electrolyzers, fuel cells and hydrogen appliances. Each home would use electricity and hydrogen. It would have its own electrolyser unit requiring water and electricity to produce hydrogen for household appliances and personal vehicles. A fuel cell running on hydrogen would run in cogeneration mode providing heat and electricity for the home. If the fuel cell had excess capacity it could feed into the grid. If reversible fuel cell technology was adequate, electrolyzers would not be needed and either the home or the car could be run from reversible fuel cells. Industry too, would be able to operate on a similar model, using local clean energy sources, and fuel cells to power production plants.
- A DC-based grid both in individual homes and between homes was envisioned. Hydrogen would be the fuel supply for home heating, cooking and air conditioning. Appliances would use catalytic burning to replace open flame natural gas systems.
- A model for decentralised wealth creation was developed also based on the premise that "small is beautiful." In this model a non-hierarchical society with sapiential authority taking precedence over structural authority was envisioned. The implications were that we wouldn't have to "go to work" to work, or to school to learn, that most things could be done from home. Movement of information, which would lead to greater energy efficiency, would replace movement of matter. In such a model technologies would have to be flexible, however, inappropriate investment would be avoided

GROUP PRIORITY TECHNOLOGIES FOR 2030-2050

The group was asked to list all the technologies pertaining hydrogen technology that they felt to be important in the 2030-2050 time frame and then rank them using a multi-voting process. The results are shown as a list of the overall top-ranked technologies. To ensure that no ideas were lost all a complete listing is shown ranked by topic area. The number of multivotes is shown in brackets.

Overall Top-Ranked Technologies

- Develop lightweight, rapid adsorption/release, high-energy density materials for transportation (7)
- Develop reversible cells for use in cars, ships etc. (5)
- Find a process to develop hydrogen from nuclear sources, having solved the problems of nuclear waste (4)
- Develop slush hydrogen, superconducting magnets etc. for hydrogen storage (4)

- Develop storage technologies for gaseous/liquid fuels in general. Technologies for liquid natural gas could be applied to hydrogen (4)
- Develop hybrid systems using fuel cells, gas turbines, new hybrid fuels (e.g. diesel plus hydrogen fuel-98% diesel, 2% hydrogen or vice versa depending on the load for use in a 50% efficient engine, ensure that particulates have been removed-particulates < 2 microns are considered carcinogenic) (4)
- Develop electrochemical methodology for reduction of carbon dioxide emissions (4)
- Develop intelligent controls for mobile/residential power sources (4)

Technologies Ranked According to Type and Perceived Importance

Production Technologies

- Develop reversible cells for use in cars, ships etc. (5)
- Find a process to develop hydrogen from nuclear sources, having solved the problems of nuclear waste (4)
- Develop closed-loop methanol and methane fuel cells (3)
- Develop better hydrogen generation bacteria (3)
- Produce hydrogen from short-cycle biomass (3)
- Develop photoelectrochemical cells (3)
- Develop better materials for high temperature
- Develop improved materials for photovoltaics for hydrogen production in an open, balanced cycle (1)
- Develop closed-cycle hydrogen production process from fermentation of waste e.g. from algae in deep shafts (1)
- Mine Arctic methane deposits (1)
- Through process analysis develop clever cogenerational systems (0)

Storage Technologies

- Develop lightweight, rapid adsorption/release, high-energy density materials for transportation (7)
- Develop slush hydrogen, superconducting magnets etc. for hydrogen storage (4)
- Develop storage technologies for gaseous/liquid fuels in general. Technologies for liquid natural gas could be applied to hydrogen (4)
- Use Canada's expertise in thermodynamics to develop novel liquefaction cycles/technologies for fuel export e.g. develop hydrogen logs for export to Japan (3)

Transportation Technologies

- Develop transportation technologies in general (3)
- Develop high-power electrical transmission by microwave over long distances (0)
- Develop intelligent sensors and controls for transmission (0)

Usage Technologies

- Develop hybrid systems using fuel cells, gas turbines, new hybrid fuels (e.g. diesel plus hydrogen fuel-98% diesel, 2% hydrogen or vice versa depending on the load for use in a 50% efficient engine, ensure that particulates have been removed-particulates < 2 microns are considered carcinogenic) (4)
- Develop underground vehicles that run on fuel cells (3)
- Develop DC technologies e.g. hydrogen-fuelled appliances, inverter technologies (3)
- Use hydrogen flames for fog dispersal (0)

Other

- Develop electrochemical methodology for reduction of carbon dioxide emissions (4)
- Develop intelligent controls for mobile/residential power sources (4)
- Develop bacterial sequestration technology (3)
- Develop sequestration technologies in the gas patch (2)
- Use expertise of advanced materials groups (2)
- Adapt gas patch technologies and expertise to purify hydrogen e.g. smart membrane technology (0)
- Develop flanking strategy for development of a hydrogen infrastructure in Canada: value-added products, applications, suitable exports (e.g. air conditioning systems based on hydrogen adsorption/absorption (no liquid involvement) (0)